

# PATENT SPECIFICATION

1,113,619

NO DRAWINGS.

The inventor of this invention in the sense of being the deviser thereof within the meaning of Section 16 of the Patents Act 1949, is:— ERNST KOCHENDOERFER, a citizen of the Federal Republic of Germany, residing at 6 Neunkirchener Strasse, Ludwigshafen/Rhein; Federal Republic of Germany.

1,113,619



Date of Application and filing Complete Specification:  
23 Sept., 1965.

No. 40528/65.

Application made in Germany (No. B78647 IVb/12o) on  
24 Sept., 1964.

Complete Specification Published: 15 May, 1968.  
© Crown Copyright 1968.

Index at Acceptance:—C2 C2B36.

Int. CL:—C 07 c 131/02.

*BEST AVAILABLE COPY*

## COMPLETE SPECIFICATION.

### Production of Oximes of Cycloaliphatic Ketones.

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to a new method for the production of oximes of cycloaliphatic ketones in an alkaline medium.

10 Oximes of cycloaliphatic ketones are usually first prepared in an acid medium and the reaction mixture is not neutralised until it is processed. Methods have however been described in which oximes of cycloaliphatic ketones have been prepared in an alkaline medium. Thus a method is known in which oximes of cycloaliphatic ketones having at least twelve carbon atoms are prepared in a heterogeneous reaction mixture containing an aqueous phase and an organic phase by the action of hydroxylamine on the ketones at elevated temperatures in such a way that a pH value of 6 to 14 is maintained in the reaction mixture during the reaction and the aqueous phase contains at least 10% by weight of salt at the end of the reaction. When carrying out this method under the prior art conditions and using ammonia as the agent for setting up the basic medium, difficulties are encountered in that the reaction proceeds fairly slowly and a considerable amount of hydroxylamine is not reacted. On the other hand, ammonia is the preferred base because

15

20

25

30

35

the ammonium salt obtained as byproduct is more desirable than analogous alkali metal salts. If unreacted hydroxylamine salt remains in the ammonium salt, however, it is necessary to carry out an additional special purification process for the ammonium salt. Another difficulty is that in many cases a cycloalkanoneoxime is obtained which includes a certain amount of cycloalkanone.

40 We have now found that oximes of cycloaliphatic ketones are obtained with higher space-time yields and/or with more extensive exhaustion of the hydroxylamine content in the aqueous phase and/or practically free from the corresponding ketones than in the prior art methods, by reacting cycloaliphatic ketones with hydroxylamine or hydroxylammonium salts in an aqueous-ammoniacal heterogeneous medium and carrying out the reaction under an ammonia pressure of more than 1 atmosphere and using ammonia in an excess of at least 50 mole% per mole of cycloalkanone.

45 Cycloalkanones, such as cyclopentanone and cyclohexanone, may be converted into the corresponding oximes by the new process. The process is particularly suitable, however, for the oximation of higher cycloalkanones, such as cyclooctanone and cyclododecanone, or generally of cycloalkanones having eight or more carbon atoms, particularly eight to twelve carbon atoms, in the ring.

50 55 60 65 70 The hydroxylamine is advantageously used in the form of an aqueous solution of a salt, for example the chloride, particularly the sulphate. Hydroxylamine is then liber-

[Price 4s. 6d.]

ated from the salt in the reaction mixture by addition of ammonia. Aqueous hydroxyl-ammonium salt solutions of 2 to 40% by weight strength may for example be used.

5 It is an advantage of the process that very dilute hydroxylammonium salt solutions may be used which contain for example 2 to 12% by weight of hydroxyl ammonium salt. Instead of liberating hydroxylamine from the salt in the reaction mixture, it is of course, also possible to start with an aqueous solution of hydroxylamine of corresponding concentration.

10 According to the invention, ammonia is used under a pressure of more than one atmosphere. It is not in general necessary to use ammonia pressures of more than 25 atmospheres. It is advantageous to use a pressure of from 1 to 10 atmospheres gauge.

15 The ammonia is used with a quantitative excess of at least 50 mole% over the cycloalkanone. It is advantageous to use an excess of 100 to 500 mole%; it is however possible to use even greater excesses, for example 1200 mole%, because recovery of ammonia is very easy during processing.

20 The hydroxylamine or hydroxylammonium salt and the cycloalkanone are in general used in about stoichiometric amounts; an excess, for example of 10 to 100%, of one or other component may however be used. It is advantageous to carry out the reaction in two or more stages by the countercurrent principle, a ketone in excess being reacted with a dilute hydroxylamine solution in one stage and an excess of hydroxylamine with the ketone in the others.

25 Although oximation will proceed at room temperature with appreciable speed, it is advantageous, in the interests of rapid reaction, to carry out the reaction at a temperature of 50° to 100°C, in particular at 70° to 100°C.

30 The process may be carried out in the presence of an organic solvent for the oxime which is inert and immiscible with water. This method has advantages in the production of cycloalkanone oximes of high cycloalkanones which are precipitated in solid form in the absence of such solvents, for example cyclododecanone oxime. Moreover the coemployment of organic solvents is recommendable when working with an excess of hydroxylamine because in this case, in the absence of solvents, there is a risk during the deposition of the solid cycloalkanone oxime or the salt that hydroxylammonium salt or ammonium salt may include unreacted cycloalkanone.

35 The following are examples of classes of organic solvents which have proved to be suitable: alkanes, cycloalkanes, aromatic hydrocarbons, alcohols, ethers, particularly those having boiling points or boiling ranges

40 within the limits 40° to 150°C at atmospheric pressure. Mixtures of solvents may also be used. Examples of suitable solvents are: n-octane, hydrocarbon mixtures boiling between 100° and 150°C from petroleum fractions, cyclohexane, methylcyclohexane, cyclooctane, benzene, toluene, xylenes, ethylbenzene, butanols, amyl alcohol, diethyl ether, glycol dimethyl ether and diisobutyl ether.

45 The solvent is generally used in an amount which is sufficient to take up the cycloalkanone oxime formed. Ratios of cycloalkanone to solvent of 1:0.3 to 1:3 are sufficient as a rule.

50 The process may be carried out for example by heating the cycloalkanone and the hydroxylammonium salt solution, if desired in the presence of an organic solvent, with ammonia, advantageously with good mixing, in an autoclave to the reaction temperature. As a rule the reaction is completely over after ten to a maximum of sixty minutes.

55 To work up the reaction mixture the pressure is released. The ammonia which escapes may be used again. In most cases however, it is used to neutralise the acid solution obtained in the Beckmann rearrangement of the cycloalkanone oxime in the further processing of the cycloalkanone oxime to lactam.

60 The process may be carried out continuously, advantageously in a cascade of stirred pressure containers, by the countercurrent principle. The procedure may be for example as follows:

65 Fresh cyclododecanone is reacted, preferably in a molar ratio of 2:1 with hydroxylamine (in the form of a hydroxylamine sulphate solution) which in part has originated from subsequent stages and in part has been freshly supplied, at 80°C for a residence time of twenty minutes in the presence of 1.5 times the amount of ammonia with reference to the ketone. After the phases of the reaction mixture have been separated, the aqueous phase is supplied to the recovery of ammonium sulphate and the organic phase, which consists of a mixture of ketone and oxime, is reacted in a second stage with fresh commercial hydroxylammonium sulphate solution, preferably in a molar ratio of 1:2. Ammonia is added in a molar excess of 120% with reference to the ketone and a solvent is added. The residence time may be for example thirty minutes at 80° to 90°C. The reaction mixture leaving the second stage is again separated into its two phases, the aqueous phase being supplied to the first stage and the organic phase being directly worked up, for example extracted with sulphuric acid. The remaining solvent is returned to the second stage. In this way it is possible for example to convert cyclododecanone in more than 99% yield into its

oxime, a saturated ammonium sulphate solution which contains less than 0.05% of hydroxylamine being obtained as byproduct.

5 The invention is illustrated by the following Examples.

The parts specified in the Examples are by weight, unless otherwise stated. Parts by weight bear the same relation to parts by volume as the gram to the litre.

10 Example 1

A mixture of 92 parts of cyclododecanone, 95 parts of cyclooctane, 8.3 parts of hydroxylammonium sulphate, 45.6 parts of ammonium sulphate, 310 parts of water and 20 parts of ammonia is heated at 110°C for sixty minutes in a stirred autoclave having a capacity of 1 part by volume and provided with a high speed stirrer, a pressure of 7 atmospheres gauge being thus set up.

20 Two phases form on cooling, the organic phase is separated, and 19.35 parts of cyclododecanone oxime (i.e. 98.3% of the theory with reference to a hydroxylamine added) are isolated from it by crystallisation. 0.05 part of hydroxylammonium sulphate may be detected titrimetrically in the aqueous layer; this is equivalent to 0.66% of the amount added. The space-time yield of cyclododecanone oxime is 464 g per litre per day. If 4 parts of ammonia be used instead of 20 parts, under otherwise identical conditions, 16.5 parts of cyclododecanone oxime and 1.0 part of unreacted hydroxylammonium sulphate are obtained. This corresponds to 84% and 12% respectively of the theory, with reference to hydroxylamine added. The space-time yield of cyclododecanone oxime is 396 g per litre of reaction space per day.

40 Example 2

A mixture of 91 parts of cyclododecanone, 16.4 parts of hydroxylammonium sulphate, 39.6 parts of ammonium sulphate, 100 parts of water and 14.9 parts by weight of ammonia is heated at 70°C for sixty minutes in a stirred autoclave having a capacity of 1 part by volume, a pressure of 6 atmospheres gauge being thus set up. On cooling, the organic phase of the reaction mixture separates and solidifies to a crystalline product from which 37.5 parts of cyclododecanone oxime and 54.9 parts of unreacted cyclododecanone are isolated. The aqueous phase contains 0.075 part of hydroxylamine. The yield of cyclododecanone oxime is 94.4% with reference to hydroxylammonium sulphate used. 0.075 part of hydroxylamine sulphate, or 0.46%, is unreacted. The space-time yield of cyclododecanone oxime is 900 g per litre per day.

Example 3

A mixture of 45.5 parts of cyclododecan-

one, 49.3 parts of cyclododecanone oxime, 41.0 parts of hydroxylammonium sulphate, 110 parts of water, 95 parts of cyclooctane and 21.3 parts of ammonia is heated for sixty minutes at 80°C in a stirred autoclave having a capacity of 1 part by volume, a pressure of 8 atmospheres gauge being thus set up. The organic phase of the reaction mixture which separates contains 98.2 parts of cyclododecanone oxime and 0.65 part of cyclododecanone. It may be used direct without purification for the production of laurolactam. The aqueous phase contains 11.4 parts of unreacted hydroxylammonium sulphate. The amount of hydroxylamine which is lacking has been decomposed under the reaction conditions. The space-time yield of cyclododecanone oxime is 2.36 kg per litre per day.

70 The same procedure is followed but only 6.8 parts of ammonia is used. 95.7 parts of cyclododecanone oxime and 2.34 parts of cyclododecanone are obtained. 18.4 parts of hydroxylamine sulphate remains unreacted. The space-time yield of cyclododecanone oxime is 2.30 kg per litre per day.

75 The same procedure is followed but only 2.55 parts of ammonia is used. The yield is further decreased to 81.4 parts of cyclododecanone oxime and 15.6 parts of cyclododecanone. 25.8 parts of hydroxylamine sulphate remains unreacted. The space-time yield of cyclododecanone oxime drops to 1.95 kg per litre per day.

80 Example 4

91 parts of cyclododecanone and 16.6 parts of hydroxylammonium sulphate in 145 parts of water are charged into a stirred autoclave, 14.9 parts of gaseous ammonia is forced in and the whole is stirred for thirty minutes at 70°C a pressure of 3 atmospheres gauge being thus set up. 37.8 parts of cyclododecanone oxime and 54.9 parts of unreacted cyclododecanone are obtained by working up. 0.075 part of hydroxylammonium sulphate remains unreacted in the aqueous phase. The space-time yield is 4.9 kg per litre of reaction space per day. 100 The yield is 94.4% of the theory with reference to reacted hydroxylammonium sulphate. 0.46% of the hydroxylammonium sulphate used remains unreacted.

105 If, for the sake of a comparison, a vigorous stream of ammonia be led without using superatmospheric pressure, through the same mixture at 70°C while it is powerfully stirred, and these reaction conditions are maintained for sixty minutes, 31.76 parts of cyclododecanone oxime and 0.9 part of unreacted hydroxylammonium sulphate are obtained by working up. In other reaction periods, the following results are obtained; RT = reaction time in minutes; CDO = 120 parts of cyclododecanone oxime; HS = 125

parts of unreacted hydroxylammonium sulphate; STY = space-time yield in kg per litre of reaction space per day:—

	RT	CDO	HS	STY
5	30	25.5	3.3	2.75
	60 (see above)	31.76	0.9	1.72
	90	32.5	0.16	1.17
10	120	36.4	0.13	0.98
	150	36.5	0.05	0.79

**WHAT WE CLAIM IS:—**

1. A process for the production of oximes of cycloaliphatic ketones by reaction of the ketones with hydroxylamine or hydroxylammonium salts in an aqueous-ammoniacal heterogeneous medium, wherein the reaction is carried out under an ammonia pressure of more than 1 atmosphere and ammonia is used in an excess of at least 20 50 mole% per mole of cycloalkanone.
2. A process as claimed in claim 1 wherein cyclododecanone is used as the cycloaliphatic ketone.
- 25 3. A process as claimed in claim 1 or 2 wherein the reaction is carried out in the presence of an organic solvent which is not miscible with water.

4. A process as claimed in any of claims 1 to 3 wherein the process is carried out countercurrently.

30

5. A process as claimed in any of claims 1 to 4 wherein hydroxylammonium sulphate is used.

35

6. A process as claimed in any of claims 1 to 5 in which the ammonia is used under a pressure of 1 to 10 atmosphere gauge.

7. A process as claimed in any of claims 1 to 6 wherein the excess of ammonia is 100 to 500 mole%.

40

8. A process as claimed in any of claims 1 to 7 carried out at from 50° to 100°C.

9. A process as claimed in any of claims 1 to 8 carried out at from 70° to 100°C.

10. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

45

11. Oximes when obtained by the process claimed in any of claims 1 to 10.

J. Y. and G. W. JOHNSON,  
Furnival House,  
14-18 High Holborn,  
London, W.C.1.  
Chartered Patent Agents.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1968.  
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,  
from which copies may be obtained.